PHYSICAL REVIEW VOLUME 129, NUMBER 2 15 JANUARY 1963

# Quantum Statistical Mechanics of a Many-Body System with Several Components

R. K. PATHRIA *and* M. P. KAWATRA

*Department of Physics, University of Delhi, Delhi, India*

(Received 24 January 1962; revised manuscript received 3 August 1962)

The binary collision method of Lee and Yang is extended in order to investigate the statistical mechanics of a multicomponent mixture of interacting gases obeying Bose-Einstein or Fermi-Dirac statistics. First, the case of a mixture of two kinds of hard-sphere spinless bosons is studied and then the generalization is carried over to the case of a mixture of several components consisting of particles with arbitrary spin and statistics. An explicit derivation of the fugacity expansion, correct to the second order in the interaction parameters, is given. Expressions are derived for the second and third virial coefficients of the system and a discussion is given of the salient features of the results obtained. Finally, the case of a binary mixture, with one component consisting of bosons and the other of fermions, is considered and the phenomenon of Bose-Einstein condensation in this system is studied.

## 1. INTRODUCTION

THE problem of investigating in detail the equilibrium properties of a multicomponent many-body system is of great physical interest. Basically its importance lies in the fact that a comprehensive study of these properties leads to an understanding of the interactions operating between particles of different kinds. Such an understanding, however, becomes possible only when one compares the experimental results with those obtained theoretically on the basis of a certain assumed law of interaction. Whereas the experimental studies of mixtures have been, and are being, carried out rather extensively, the corresponding theoretical investigations have remained relatively at a low ebb. Nevertheless some such treatments did appear in the past but almost invariably they were based on the principles of classical statistical mechanics.

A schematic study on the classical lines of the statistical thermodynamics of a system composed of several components which do not react chemically was made by McMillan and Mayer[1] who carried out their investigation on the basis set previously by the pioneering work of Mayer and his collaborators[2] on the problem of imperfect gases and their condensation.

The first attempt to treat systematically the problem of a multicomponent system on the principles of quantum statistical mechanics was made by Band[3] who, closely following the work of McMillan and Mayer, carried out an investigation into the properties of mixtures of Bose-Einstein and Fermi-Dirac fluids. He thereby expressed the distribution functions of the problem in terms of "irreducible integrals," formally identical with the ones given by McMillan and Mayer although their physical significance, due to the presence of degeneracy factors, was not quite the same. However, the final formulas so obtained were rather too general in nature to permit a quantitative interpretation, essentially because the results could not be expressed in explicit terms unless the integrals involved were actually evaluated. The quantum-mechanical problem of mixtures has thus remained almost unsolved insofar as the explicit derivation of the equation of state and of expressions for the various thermodynamical properties of the system is concerned.

Recently, Lee and Yang[4] have developed a systematic method of studying the statistical mechanics of a low-density gaseous system of interacting particles in which quantum effects are important. The essential feature of their treatment is to first separate out the effects of the quantum statistics of the problem by expressing the grand partition function of the system under study in terms of certain functions (the cluster functions) defined for a corresponding quantum-mechanical problem with Boltzmann statistics. Next, these functions are expressed, in the form of something like a power series, in terms of a binary kernel which, in turn, is obtainable from a solution of the relevant two-body problem. Discussing in detail the case of a single-component system composed of hard spheres, Lee and Yang have demonstrated how their method can be applied in order to derive explicit expressions for the various thermodynamical properties of the system.

We find that the method developed by Lee and Yang, referred to as the binary collision method, can be readily employed for investigating quantum mechanically the equilibrium properties of low-density gaseous mixtures. First, we study the case of a simple two-component system of interacting particles. In Sec. 2 the problem is formulated in the language of cluster operators $U_{ll^*}{}^{q}$, which are the quantum-statistical counterparts of the

[1] W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945); see also J. E. Mayer, J. Phys. Chem. **43**, 71 (1939). For earlier work, see R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, New York, 1936), Chaps. VIII–X.

[2] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937); J. E. Mayer and P. G. Ackermann, *ibid.* **5**, 74 (1937); see also, J. E. Mayer and S. F. Harrison, *ibid.* **6**, 87, 101 (1938).

[3] W. Band, J. Chem. Phys. **16**, 343 (1948).

[4] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959); **116**, 25 (1959). These two papers are referred to in the text as LYI and LYII, respectively.

corresponding classical Ursell functions. In Sec. 3 we frame the rule which enables one to express the functions $U_{ll^*}{}^q$ in terms of the functions $U_{nn^*}$ defined for a quantum-mechanical Boltzmannian mixture. In Sec. 4 the functions $U_{nn^*}$ are expanded in the powers of three binary kernels appropriate for a two-component system and further, explicit expressions are derived for these kernels in the case of particles (like or unlike) interacting through a hard-sphere potential. In Sec. 5 an explicit derivation of the fugacity expansion, to the second order in the interaction parameters, is carried out for the case of a mixture of two kinds of hard-sphere spinless bosons.

Next, the treatment is extended to the study of a multicomponent system. In Sec. 6 we consider the essential amplifications in the theory which are brought about by the introduction of more components into the two-component system. The additional terms appearing in the particular case of a system of hard-sphere spinless bosons are explicitly evaluated. In the next section the treatment is generalized to the case where the particles obey arbitrary statistics and have spins of arbitrary values (of course, in conformity with the respective statistics). The complete fugacity expansion, to the second order in the interaction parameters, is then derived for this generalized system. In Sec. 8 explicit expressions are obtained for the second and third, pure and mixed, virial coefficients of the system. The salient features of the various results of this investigation are discussed at some length and also the question of the application of these results to systems with interactions more realistic than the hard-sphere one is briefly considered.

A detailed investigation into the low-temperature behavior of a binary mixture of a Bose gas and a Fermi gas is indeed of great physical interest, especially because of its possible bearing on the problem of $He^3-He^4$ mixtures. However, the theory as such is not suited for this investigation because it fails to treat the system in the region of the lambda transition. In fact, a reformulation of the theory in terms of average occupation numbers in momentum space, along the lines suggested by the later work of Lee and Yang,[5] is essential before this particular problem can be tackled successfully by the binary collision method. This is done in Sec. 9 where the phenomenon of Bose-Einstein condensation in a Bose-Fermi mixture is considered and the expressions for the various physical properties of the system at the condensation point are obtained.

## 2. FORMULATION OF THE QUANTUM-STATISTICAL PROBLEM FOR A BINARY MIXTURE

We consider a two-component system of particles, $N$ belonging to the first component and $N^*$ to the second, moving in a cubic box of dimensions $L\times L\times L$ (volume $L^3=\Omega$), their motion conforming to periodic boundary conditions. The Hamiltonian of this system would be (with $\hbar=1$)

$$H_{NN^*}=-\frac{1}{2m}\sum_{i=1}^{N}\nabla_i^2-\frac{1}{2m^*}\sum_{i^*=1}^{N^*}\nabla_{i^*}^2+V, \qquad (1)$$

where $m$ and $m^*$ are the respective masses of the two kinds of particles, while $V$ is the potential energy operator which consists of a sum over all pairs of particles constituting the system.[6]

We introduce the (probability) operator

$$W_{NN^*}\equiv\exp(-\beta H_{NN^*}), \qquad (2)$$

where

$$\beta=(kT)^{-1}. \qquad (3)$$

The cluster operators $U_{ll^*}$ are then defined in terms of the operators $W_{nn^*}$ in the same manner as in the case of a single-component system:

$$U_{10}(1)=W_{10}(1);\quad U_{01}(1^*)=W_{01}(1^*), \qquad (4)$$

$$\begin{aligned}U_{20}(1,2)&=W_{20}(1,2)-W_{10}(1)W_{10}(2);\\ U_{11}(1,1^*)&=W_{11}(1,1^*)-W_{10}(1)W_{01}(1^*);\\ U_{02}(1^*,2^*)&=W_{02}(1^*,2^*)-W_{01}(1^*)W_{01}(2^*),\end{aligned} \qquad (5)$$

etc. It can now readily be shown that the equilibrium pressure $p$ and the (partial) particle densities $\rho$ and $\rho^*$ are given by the Mayer equations

$$p/kT=\lim_{\Omega\to\infty}\sum_{\substack{l,l^*=0\\(l+l^*)\geq 1}}^{\infty} b_{ll^*}(\Omega)z^lz^{*l^*}, \qquad (6)$$

$$\rho=\lim_{\Omega\to\infty}\sum_{\substack{l,l^*=0\\(l+l^*)\geq 1}}^{\infty} lb_{ll^*}(\Omega)z^lz^{*l^*}, \qquad (7)$$

and

$$\rho^*=\lim_{\Omega\to\infty}\sum_{\substack{l,l^*=0\\(l+l^*)\geq 1}}^{\infty} l^*b_{ll^*}(\Omega)z^lz^{*l^*}, \qquad (8)$$

where $z$ and $z^*$ are, respectively, the "activities" of the two components whereas $b_{ll^*}$ are the fugacity coefficients:

$$b_{ll^*}(\Omega)=(l!l^*!\Omega)^{-1}\,\mathrm{Tr}(U_{ll^*}). \qquad (9)$$

The definitions of the operators introduced above and the various relations existing between them remain unchanged when we go over to the limit of infinite volume. One can show that in this limit

$$\begin{aligned}b_{ll^*}(\Omega)&\to b_{ll^*}(\infty)\\ &=(l!l^*!)^{-1}\int_{-\infty}^{+\infty}\langle 0,\mathbf{r}_2,\cdots\mathbf{r}_l;\mathbf{r}_{1^*},\cdots\mathbf{r}_{l^*}|U_{ll^*}(\infty)|\\ &\qquad 0,\mathbf{r}_2,\cdots\mathbf{r}_l;\mathbf{r}_{1^*},\cdots\mathbf{r}_{l^*}\rangle\\ &\qquad\times d^3r_2\cdots d^3r_ld^3r_{1^*}\cdots d^3r_{l^*},\end{aligned} \qquad (10)$$

[5] T. D. Lee and C. N. Yang, Phys. Rev. **117**, 22 (1960); this paper is referred to in the text as LYIV.

[6] In the present investigation, interactions of an order higher than the two-body interactions are not considered.

where $U_{ll^*}(\infty)$ are the $U$ operators for $\Omega=\infty$; the integration here extends over the coordinates of $(l+l^*-1)$ particles. It may be remarked that in the foregoing integral, the position of any one of the $(l+l^*)$ particles could be taken as the origin because the validity of the result depends simply upon the fact that for one of the $(l+l^*)$ coordinates fixed, the integration of $U_{ll^*}$ over the remaining $(l+l^*-1)$ coordinates gives a result independent of the position of the fixed coordinate. This, in turn, rests on the highly plausible assumption that the effective range of interaction between two particles is much smaller than the linear dimensions of the container.

The whole program under consideration can be carried out in the momentum representation as well. For this purpose we introduce subsidiary operators $u_{ll^*}$, defined by

$$\langle \mathbf{k}_1',\cdots \mathbf{k}_l';\mathbf{k}_{1^*}',\cdots \mathbf{k}_{l^*}'|U_{ll^*}(\infty)|\mathbf{k}_1,\cdots \mathbf{k}_l;\mathbf{k}_{1^*},\cdots \mathbf{k}_{l^*}\rangle$$
$$=\delta^3\{\sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha'+\mathbf{k}_{\alpha^*}')-\sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha+\mathbf{k}_{\alpha^*})\}$$
$$\times\langle \mathbf{k}_1',\cdots \mathbf{k}_l';\mathbf{k}_{1^*}',\cdots \mathbf{k}_{l^*}'|u_{ll^*}|\mathbf{k}_1,\cdots \mathbf{k}_l;\mathbf{k}_{1^*},\cdots \mathbf{k}_{l^*}\rangle; \tag{11}$$

obviously the subsidiary operators are defined only for those momenta which satisfy the principle of momentum conservation. In terms of these subsidiary operators, the fugacity coefficients take the form

$$b_{ll^*}(\infty)=(8\pi^3 l!l^*!)^{-1}$$
$$\times\int\langle \mathbf{k}_1,\cdots \mathbf{k}_l;\mathbf{k}_{1^*},\cdots \mathbf{k}_{l^*}|u_{ll^*}|\mathbf{k}_1,\cdots \mathbf{k}_l;\mathbf{k}_{1^*},\cdots \mathbf{k}_{l^*}\rangle$$
$$\times d^{3l}k d^{3l^*}k. \tag{12}$$

All the foregoing relations are valid irrespective of the statistics obeyed by the particles. The question of the statistics assumes importance when we undertake the choice of the $(l,l^*)$-body states (in the volume $\Omega$) with respect to which the matrix elements of the various operators are formed. In the case of the probability operator (2), the matrix elements would be given by

$$\langle 1',\cdots N';1^{*\prime},\cdots N^{*\prime}|W_{NN^*}{}^q|1,\cdots N;1^*,\cdots N^*\rangle$$
$$=N!N^*!\sum_i{}'\psi_i(1',\cdots N';1^{*\prime},\cdots N^{*\prime})$$
$$\times\bar{\psi}_i(1,\cdots N;1^*,\cdots N^*)\exp(-\beta E_i), \tag{13}$$

where the superscript $q$ on $W_{NN^*}$ signifies the quantum statistics obeyed (independently of each other) by the two kinds of particles and the symbol $\sum_i{}'$ on the right-hand side implies a summation over all the states $i$ which are properly symmetrized in view of the *two* statistics involved. The corresponding relation for a system with Boltzmann statistics would be

$$\langle 1',\cdots N';1^{*\prime},\cdots N^{*\prime}|W_{NN^*}|1,\cdots N;1^*,\cdots N^*\rangle$$
$$=\sum_{\text{all } i}\psi_i(1',\cdots N';1^{*\prime},\cdots N^{*\prime})$$
$$\times\bar{\psi}_i(1,\cdots N;1^*,\cdots N^*)\exp(-\beta E_i); \tag{14}$$

now no superscript has been put on $W_{NN^*}$ and the summation also extends over all the eigenfunctions $\psi_i$. Further, the unstarred and starred integers which appear in (13) and (14) as arguments of the wave function $\psi_i$ and its complex conjugate $\bar{\psi}_i$ stand, respectively, for the coordinates of the two kinds of particles.

### 3. $U_{ll^*}{}^q$ IN TERMS OF $U_{nn^*}$

We now formulate the explicit rule which would enable us to express the cluster functions $U_{ll^*}{}^q$ pertaining to the actual quantum-statistical system in terms of the corresponding ones, $U_{nn^*}(n\leqslant l, n^*\leqslant l^*)$, for a Boltzmannian system. One can readily see that such relations for the functions $W_{nn^*}{}^q$ and $W_{nn^*}$ follow immediately from equations like (13) and (14), viz.,

$$\langle 1',\cdots n';1^{*\prime},\cdots n^{*\prime}|W_{nn^*}{}^q(1,\cdots n;1^*,\cdots n^*\rangle$$
$$=\sum_{P',P^{*\prime}}\gamma^{(P')}\gamma^{*(P^{*\prime})}P'P^{*\prime}\langle 1',\cdots n';$$
$$1^{*\prime},\cdots n^{*\prime}|W_{nn^*}|1,\cdots n;1^*,\cdots n^*\rangle, \tag{15}$$

where $P'$ is any one of the $n!$ operators that permute the variables $1', \cdots n'$, $P^{*\prime}$ is any one of the $n^*!$ operators that permute the variables $1^{*\prime}, \cdots n^{*\prime}$, symbols $(P')$ and $(P^{*\prime})$ stand for the order of the permutations (as regards their being *even* or *odd*) while $\gamma$ and $\gamma^*$ are the respective indices of symmetry for the two components (being $+1$ for a Bose-Einstein and $-1$ for a Fermi-Dirac component).

Now, the relations (15), coupled with those given by (4), (5), etc., both for the actual system and for the corresponding Boltzmannian system, enable one to eliminate the functions $W_{nn^*}{}^q$ and $W_{nn^*}$ and obtain, as eliminant, relations connecting $U_{ll^*}{}^q$ with $U_{nn^*}$. The final result can be stated in the form of the followlng rule.[7]

*Rule.* To calculate $U_{ll^*}{}^q$, we first distribute the integers $1, 2, \cdots l; 1^*, 2^*, \cdots l^*$ into various groups such that there are $m_{\alpha\alpha^*}$ groups, each containing $\alpha$ unstarred integers and $\alpha^*$ starred ones, with

$$\sum_{\alpha=1,\alpha^*=0}\alpha m_{\alpha\alpha^*}=l,$$
$$\sum_{\alpha=0,\alpha^*=1}\alpha^* m_{\alpha\alpha^*}=l^*, \tag{16}$$

$m_{\alpha\alpha^*}=0, 1, 2, \cdots$. (See, however, footnote 8.) A typical

[7] It may be mentioned here that the rule stated hereafter is valid in any representation. In particular, if one chooses to work in the momentum representation the variables $1, 2, \cdots, 1^*, 2^*, \cdots$ will stand for the particle momenta.

grouping of this sort may be represented as follows:

$$\{(a)(b)\cdots\}\{(cd)(ef)\cdots\}\{(ghi)\cdots\}\cdots$$
$$\{(jk^*)\cdots\}\{(lmn^*)\cdots\}\{(op^*q^*)\cdots\}\cdots$$
$$\{(r^*)(s^*)\cdots\}\{(t^*u^*)(v^*w^*)\cdots\}\{(x^*y^*z^*)\cdots\}\cdots, \quad (17)$$

where $a$, $b$, $\cdots$; $k^*$, $n^*$, $\cdots$ stand for the various integers. Within each round bracket the integers are arranged in an ascending order while within each curly bracket the round brackets are arranged such that their first integers follow an ascending sequence. In this arrangement the unstarred integers are at every stage to be written before the starred ones and the ordering rule given in the preceding sentence is to apply to the two kinds of integers separately.

We then form a product of operators

$$\prod_{n,n^*}\langle\tilde{p}',\tilde{q}',\cdots;\tilde{p}^{*\prime},\tilde{q}^{*\prime},\cdots|U_{nn^*}|p,q,\cdots;p^*,q^*,\cdots\rangle, \quad (18)$$

where $(\tilde{p}',\tilde{q}',\cdots)$ is any permutation of the coordinates $p'$, $q'$, $\cdots$ and similarly $(\tilde{p}^{*\prime},\tilde{q}^{*\prime},\cdots)$ that of the coordinates $p^{*\prime}$, $q^{*\prime}$, $\cdots$, while $n$ and $n^*$ run through all values available in the grouping (17); this would give $m_{nn^*}$ factors of the type $U_{nn^*}$. We then multiply the product (18) by the factor $\gamma^{(P')}\gamma^{*(P^{*\prime})}$ where $(P')$ and $(P^{*\prime})$ are the orders, as regards evenness or oddness, of the respective permutations (of all the coordinates appearing in the various bras with respect to those appearing in the kets) and then sum up over all such permutations in the bras which satisfy the condition that upon putting $\mathbf{r}'=\mathbf{r}$ for all the $(l+l^*)$ variables, the summand does not break into factors which depend upon *mutually exclusive* coordinates.[8]

Finally, we sum up all such expressions as obtained above over the different groupings (17). This total sum would be equal to $U_{ll^*}{}^q$.

*Illustration.* For a system composed of free particles, we have in the Boltzmannian case

$$\begin{aligned}\langle 1',\cdots N';1^{*\prime},\cdots N^{*\prime}|W_{NN^*}|1,\cdots N;1^*,\cdots N^*\rangle\\ =\langle 1'|W_{10}|1\rangle\cdots\langle N'|W_{10}|N\rangle\langle 1^{*\prime}|W_{01}|1^*\rangle\cdots\\ \times\langle N^{*\prime}|W_{01}|N^*\rangle.\end{aligned} \quad (19)$$

Hence, one obtains from relations (4), (5), etc.,

$$U_{nn^*}=0 \quad \text{for} \quad (n+n^*)>1. \quad (20)$$

In the case of quantum statistics we then have (see footnote 8):

$$U_{ll^*}{}^q=0, \quad (21)$$

if both $l$ and $l^*$ are nonzero. Consequently, from (9),

$$b_{ll^*}{}^q=0, \quad (22)$$

[8] This condition obviously implies that in case both $l$ and $l^*$ are nonzero, a product of the type $(U_{10}\cdots U_{10})(U_{01}\cdots U_{01})$ cannot be considered; it must contain at least one factor $U_{nn^*}$ such that both $n$ and $n^*$ are nonzero.

unless either $l=0$ or $l^*=0$. Equation (6) then leads to the result (for $\Omega\rightarrow\infty$)

$$p/kT=\sum_{l=1}^{\infty}b_{l0}{}^qz^l+\sum_{l^*=1}^{\infty}b_{0l^*}{}^qz^{*l^*}, \quad (23)$$

that is, the law of partial pressures is obeyed. An explicit evaluation of the coefficients $b_{l0}{}^q$ and $b_{0l^*}{}^q$ for the case of an ideal Bose or Fermi gas is quite straightforward.

### 4. $U_{nn^*}$ AND THE BINARY KERNELS

We first note that the functions $U_{nn^*}$ and $W_{nn^*}$ can be given a diagrammatic representation in the same manner as the corresponding functions for a single-component system. Further, the functions $U_{nn^*}$ can be expressed in terms of a set of binary kernels (three in the present case), again on the same lines as in the pure case. Equations (5), for instance, give

$$U_{20}(\beta)=\exp(-\beta H_{20})-\exp[(+\beta/2m)\nabla_1{}^2]\times\exp[(+\beta/2m)\nabla_2{}^2], \quad (24a)$$

$$U_{11}(\beta)=\exp(-\beta H_{11})-\exp[(+\beta/2m)\nabla_1{}^2]\times\exp[(+\beta/2m^*)\nabla_{1^*}{}^2], \quad (24b)$$

and

$$U_{02}(\beta)=\exp(-\beta H_{02})-\exp[(+\beta/2m^*)\nabla_{1^*}{}^2]\times\exp[(+\beta/2m^*)\nabla_{2^*}{}^2]. \quad (24c)$$

Defining the binary kernels by the two-body relations

$$\begin{aligned}B(\beta)&=-V\,W(\beta)\\ &=-V\exp(-\beta H),\end{aligned} \quad (25)$$

and taking into account (24), one can write

$$B(\beta;1,2)=\frac{\partial U_{20}(\beta)}{\partial\beta}-\frac{1}{2m}(\nabla_1{}^2+\nabla_2{}^2)U_{20}(\beta), \quad (26a)$$

$$B(\beta;1,1^*)=\frac{\partial U_{11}(\beta)}{\partial\beta}-\left(\frac{1}{2m}\nabla_1{}^2+\frac{1}{2m^*}\nabla_{1^*}{}^2\right)U_{11}(\beta), \quad (26b)$$

and

$$B(\beta;1^*,2^*)=\frac{\partial U_{02}(\beta)}{\partial\beta}-\frac{1}{2m^*}(\nabla_{1^*}{}^2+\nabla_{2^*}{}^2)U_{02}(\beta). \quad (26c)$$

It is clear that the binary kernels can be explicitly evaluated, with the help of (24) and (26), from the solutions of the relevant two-body problems.

$U_{nn^*}$ can now be written down in terms of the three binary kernels introduced above:

$$U_{11}(\beta)=\int_0^\beta d\beta'\,\omega(\beta-\beta';1)\omega(\beta-\beta';1^*)B(\beta';1,1^*), \quad (27)$$

and corresponding relations for $U_{20}(\beta)$ and $U_{02}(\beta)$;

$$U_{21}(\beta)=\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\,\omega(\beta-\beta'';1)\omega(\beta-\beta';2)\omega(\beta-\beta';1^*)B(\beta'-\beta'';2,1^*)B(\beta'';1,2)\omega(\beta'';1^*)$$

$$+\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\,\omega(\beta-\beta';1)\omega(\beta-\beta';2)\omega(\beta-\beta'';1^*)B(\beta'-\beta'';1,2)B(\beta'';2,1^*)\omega(\beta'';1)$$

$$+\text{four other terms of order } B^2$$

$$+\text{terms of higher order in } B, \tag{28}$$

and corresponding relations for $U_{12}(\beta)$, $U_{30}(\beta)$, and $U_{03}(\beta)$; the operators $\omega(\beta;i)$ and $\omega(\beta;i^*)$ stand for

$$W_{10}(\beta)\equiv\exp[(\beta/2m)\nabla_i^2],$$

and

$$W_{01}(\beta)\equiv\exp[(\beta/2m^*)\nabla_{i^*}^2],$$

respectively. Equations similar to (27) and (28) can also be written down for higher values of $n$ and $n^*$.

It may be noted that the foregoing equations, being operator equations, are valid in any representation.

We now evaluate explicitly the binary kernels (26) in the particular case when the two-body interaction between the particles constituting the system is of the hard-sphere type. If we denote the hard-sphere diameters by $a$, $a^*$, and $\bar{a}$ in the case of particles of the first component, of the second component and the unlike ones,[9] respectively, then the three kernels to be evaluated are

$B_{20}(\beta;i,j)$, with parameters $m$ and $a$,

$B_{11}(\beta;i,i^*)$, with parameters $m$, $m^*$, and $\bar{a}$,

and

$B_{02}(\beta;i^*,j^*)$, with parameters $m^*$ and $a^*$.

We give here the result for the "mixed" kernel $B_{11}$; those for the "pure" ones, $B_{20}$ and $B_{02}$, then follow directly from that for $B_{11}$ by equating $m$ and $m^*$ and replacing $\bar{a}$ by $a$ or $a^*$ as the case may be.

Carrying out the necessary calculations in the momentum representation, we obtain, in the mixed case, the following expression for the $S$-state contribution to the matrix elements of $U_{11}$:

$$\begin{aligned}\langle \mathbf{k}_1',\mathbf{k}_{1^*}'|U_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle &= \delta^3(\mathbf{k}_1'+\mathbf{k}_{1^*}'-\mathbf{k}_1-\mathbf{k}_{1^*})[4\pi^2k'k(k'^2-k^2)]^{-1}\{\sin(k'+k)\bar{a}[k'\exp(-\beta E')-k\exp(-\beta E)]\\ &\quad -\sin(k'-k)\bar{a}[k'\exp(-\beta E')+k\exp(-\beta E)]+(4/\pi)^{1/2}[\cos(k'+k)\bar{a}-\cos(k'-k)\bar{a}]\\ &\quad \times[k'M(\beta k'^2/2\mu)^{1/2}\exp(-\beta E')-kM(\beta k^2/2\mu)^{1/2}\exp(-\beta E)]\},\end{aligned} \tag{29}$$

where

$$\mathbf{k}'=\mu(\mathbf{k}_1'/m-\mathbf{k}_{1^*}'/m^*),\quad \mathbf{k}=\mu(\mathbf{k}_1/m-\mathbf{k}_{1^*}/m^*), \tag{30}$$

$$\mu=mm^*/(m+m^*), \tag{31}$$

$$E'=k_1'^2/2m+k_{1^*}'^2/2m^*,\quad E=k_1^2/2m+k_{1^*}^2/2m^*, \tag{32}$$

and

$$M(y)=\int_0^y \exp(x^2)dx. \tag{33}$$

Using (29) and the relation (26b) written in the momentum representation,

$$\langle \mathbf{k}_1',\mathbf{k}_{1^*}'|B_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle=\frac{\partial}{\partial\beta}\langle \mathbf{k}_1',\mathbf{k}_{1^*}'|U_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle+E'\langle \mathbf{k}_1',\mathbf{k}_{1^*}'|U_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle, \tag{26b'}$$

one obtains for $B_{11}$, correct to second order in $\bar{a}$,

$$\begin{aligned}\langle \mathbf{k}_1',\mathbf{k}_{1^*}'|B_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle &= -\frac{\bar{a}}{4\pi^2\mu}\delta^3(\mathbf{k}_1'+\mathbf{k}_{1^*}'-\mathbf{k}_1-\mathbf{k}_{1^*})\exp(-\beta E)+\frac{\bar{a}^2}{2\pi^{5/2}\mu}\delta^3(\mathbf{k}_1'+\mathbf{k}_{1^*}'-\mathbf{k}_1-\mathbf{k}_{1^*})\exp(-\beta E)\\ &\quad \times k\{M(\beta k^2/2\mu)^{1/2}-\tfrac{1}{2}(\beta k^2/2\mu)^{-1/2}\exp(\beta k^2/2\mu)\}.\end{aligned} \tag{34}$$

[9] Indeed, in the case of hard-sphere interaction $\bar{a}=\frac{1}{2}(a+a^*)$. For the sake of generality, however, we are retaining here the independent symbol $\bar{a}$, especially in view of the possible extension of the present treatment to cases involving more realistic interactions.

From the foregoing expression, one can readily write down corresponding expressions for the pure kernels $B_{20}$ and $B_{02}$.

## 5. FUGACITY EXPANSION FOR A BINARY MIXTURE OF HARD-SPHERE SPINLESS BOSONS

We are now in a position to evaluate explicitly, to the second order in the interaction parameters, the fugacity expansion for a two-component system composed of hard-sphere bosons. In the following treatment the particles will be assumed spinless.

It is most natural to split the fugacity series into three parts, viz.,

$$\sum_{\substack{l,l^*=0\\(l+l^*)\geq 1}}^{\infty} b_{ll^*}{}^q z^l z^{*l^*} = \sum_{l=1}^{\infty} b_{l0}{}^q z^l + \sum_{l^*=1}^{\infty} b_{0l^*}{}^q z^{*l^*} + \sum_{l,l^*=1}^{\infty} b_{ll^*}{}^q z^l z^{*l^*}. \quad (35)$$

Results for the first two parts follow directly from the calculations of Lee and Yang[4] (see LYII) for a single-component system of bosons:

$$\sum_{l=1}^{\infty} b_{l0}{}^q z^l = \lambda^{-3}[g_{5/2}(z) - 2\{g_{3/2}(z)\}^2(a/\lambda) + 8g_{1/2}(z)\{g_{3/2}(z)\}^2(a/\lambda)^2 + 8F(z)(a/\lambda)^2 + O(a/\lambda)^3], \quad (36)$$

and

$$\sum_{l^*=1}^{\infty} b_{0l^*}{}^q z^{*l^*} = \lambda^{*-3}[g_{5/2}(z^*) - 2\{g_{3/2}(z^*)\}^2(a^*/\lambda^*) + 8g_{1/2}(z^*)\{g_{3/2}(z^*)\}^2(a^*/\lambda^*)^2 + 8F(z^*)(a^*/\lambda^*)^2 + O(a^*/\lambda^*)^3], \quad (37)$$

where

$$g_n(x) = \sum_{i=1}^{\infty} i^{-n} x^i, \quad (38)$$

and

$$F(x) = \sum_{r,s,t=1}^{\infty} (rst)^{-1/2}(r+s)^{-1}(s+t)^{-1} x^{r+s+t}, \quad (39)$$

while $\lambda$ and $\lambda^*$ are the respective thermal wavelengths given by

$$\lambda = (2\pi\beta/m)^{1/2} \quad \text{and} \quad \lambda^* = (2\pi\beta/m^*)^{1/2}. \quad (40)$$

In order to calculate the third part in (35) we recall (12) and (11); thus, one has to consider the functions $U_{ll^*}{}^q$ for $l$, $l^* \geqslant 1$. Now, by virtue of the rule formulated in Sec. 3, we have (for $\gamma=\gamma^*=1$)

$$\begin{aligned} U_{ll^*}{}^q =& \sum\{U_{10}\cdots U_{10}\}\{U_{11}\}\{U_{01}\cdots U_{01}\} \\ &+\sum\{U_{10}\cdots U_{10}\}\{U_{11}U_{11}\}\{U_{01}\cdots U_{01}\} \\ &+\sum\{U_{10}\cdots U_{10}\}\{U_{20}\}\{U_{11}\}\{U_{01}\cdots U_{01}\} \\ &+\sum\{U_{10}\cdots U_{10}\}\{U_{11}\}\{U_{01}\cdots U_{01}\}\{U_{02}\} \\ &+\sum\{U_{10}\cdots U_{10}\}\{U_{21}\}\{U_{01}\cdots U_{01}\} \\ &+\sum\{U_{10}\cdots U_{10}\}\{U_{12}\}\{U_{01}\cdots U_{01}\} \\ &+\text{terms of higher order.} \end{aligned} \quad (41)$$

The summations in (41) are to be carried over all *permissible* permutations of the variables appearing in the bras of the matrix elements of the various factors here. We evaluate the contributions to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ from the various sums in (41), one by one. Calculations for this purpose are done throughout in the momentum representation.

I. Consider a typical term in the first sum:

$$\{U_{10}\cdots U_{10}\}\langle i',i^{*\prime}|U_{11}|1,1^*\rangle\{U_{01}\cdots U_{01}\}. \quad (42)$$

In order to first compute its contribution to $u_{ll^*}{}^q$, defined in (11), we notice that (42) contains $(l+l^*-1)$ $\delta^3$ functions. The one from $U_{11}$ can be replaced, through the use of the other $\delta^3$ functions, by

$$\delta^3\{\sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha'+\mathbf{k}_{\alpha^*}') - \sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha+\mathbf{k}_{\alpha^*})\},$$

which has to be dropped while going from $U_{ll^*}{}^q$ to $u_{ll^*}{}^q$. One then uses (12) and first, with the help of the $(l+l^*-2)$ $\delta^3$ functions coming from the factors $U_{10}$ and $U_{01}$, carries out the integration over $(l+l^*-2)$ momentum variables, thus leaving an integration over $\mathbf{k}_1$ and $\mathbf{k}_{1^*}$. The contribution to $b_{ll^*}{}^q$ from the typical term (42) is, therefore, of the form[10]

$$(8\pi^3 l!l^*!)^{-1}\int\langle\mathbf{1},\mathbf{1}^*|u_{11}|\mathbf{1},\mathbf{1}^*\rangle \times\exp\{-\beta[(l-1)E(\mathbf{1})+(l^*-1)E(\mathbf{1}^*)]\}, \quad (43)$$

where

$$E(\mathbf{k}) = k^2/2m \quad \text{and} \quad E(\mathbf{k}^*) = k^{*2}/2m^*. \quad (44)$$

Since the permutations in the bras of the various factors in (42) are to be done among the unstarred and the starred variables separately, the total number of terms of the type (43) will be $l!l^*!$. Thus, the total contribution to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ from the first sum in (41) would be

$$s_1 = (8\pi^3)^{-1}\int\langle\mathbf{1},\mathbf{1}^*|u_{11}|\mathbf{1},\mathbf{1}^*\rangle\mathfrak{M}(\mathbf{1})\mathfrak{M}(\mathbf{1}^*), \quad (45)$$

where

$$\mathfrak{M}(\mathbf{k}) = z\{1-z\exp[-\beta E(\mathbf{k})]\}^{-1}, \quad (46)$$

and

$$\mathfrak{M}(\mathbf{k}^*) = z^*\{1-z^*\exp[-\beta E(\mathbf{k}^*)]\}^{-1}. \quad (47)$$

The evaluation of (45) can be done by taking the

---

[10] Henceforth, we use the notation $\mathbf{1}\equiv\mathbf{k}_1$, $\mathbf{1}^*\equiv\mathbf{k}_{1^*}$, etc., and the convention that an integral sign not followed by any differential is meant to represent an integration over all the momentum variables appearing in the integrand.

diagonal elements of the matrix $u_{11}$ in the form [see (29)]

$$\langle 1,1^*|u_{11}|1,1^*\rangle = -\frac{\bar{a}}{4\pi^2\mu}\beta\exp\{-\beta[E(1)+E(1^*)]\} - \frac{\bar{a}^2}{2\pi^{5/2}}\frac{1}{k}\exp\left(-\beta\frac{(1+1^*)^2}{2(m+m^*)}\right)$$
$$\times\{(\beta k^2/2\mu)^{1/2}+(1-\beta k^2/\mu)M(\beta k^2/2\mu)^{1/2}\exp(-\beta k^2/2\mu)\}+O(\bar{a}^3). \quad (48)$$

The quantities $k$ and $\mu$ appearing here have already been defined in (30) and (31). Carrying out the integrations in (45), one obtains

$$s_1 = -\bar{a}(mm^*)^{1/2}(m+m^*)(2\pi\beta)^{-2}g_{3/2}(z)g_{3/2}(z^*) - 4\bar{a}^2 mm^*(m+m^*)^{1/2}(2\pi\beta)^{-5/2}\sum_{r,s=1}^{\infty} z^r z^{*s}(rs)^{-2}\left(rs-\frac{mr+m^*s}{m+m^*}\right)^{1/2}, \quad (49)$$

correct to the second order in $\bar{a}$.

II. Let us now consider any term in the second sum in (41). Here again one of the two $\delta^3$ functions associated with the factors $U_{11}$ can be written, with the help of other such functions present in the product, as

$$\delta^3\Big[\sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha'+\mathbf{k}_{\alpha^*}')-\sum_{\alpha,\alpha^*}(\mathbf{k}_\alpha+\mathbf{k}_{\alpha^*})\Big]$$

and dropped in going over to $u_{ll^*}{}^q$. We are now left with $(l+l^*-4)$ $\delta^3$ functions associated with the factors $U_{10}$ and $U_{01}$ and one $\delta^3$ function with the other factor $U_{11}$. Consequently, $(l+l^*-4)$ integrations can be done straightaway, leaving thereby an integral over the remaining four momentum variables with the integrand containing one $\delta^3$ function. It is not difficult to see that the contribution from this sum to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ is given by

$$s_2 = s_{21}+s_{22}+s_{23}, \quad (50)$$

where

$$s_{21} = \tfrac{1}{2}(8\pi^3)^{-1}\int\langle 1,1^*|u_{11}|1,2^*\rangle\langle 2,2^*|u_{11}|2,1^*\rangle\delta^3(1^*-2^*)\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)\mathfrak{M}(2^*), \quad (51)$$

$$s_{22} = \tfrac{1}{2}(8\pi^3)^{-1}\int\langle 1,1^*|u_{11}|2,1^*\rangle\langle 2,2^*|u_{11}|1,2^*\rangle\delta^3(1-2)\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)\mathfrak{M}(2^*), \quad (52)$$

and

$$s_{23} = \tfrac{1}{2}(8\pi^3)^{-1}\int\langle 1,1^*|u_{11}|2,2^*\rangle\langle 2,2^*|u_{11}|1,1^*\rangle\delta^3(1+1^*-2-2^*)\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)\mathfrak{M}(2^*). \quad (53)$$

In view of the $\delta^3$ functions appearing in (51) and (52), it is only the diagonal elements of the operators $u_{11}$ that are needed, and those too only in the first order of approximation in $\bar{a}$. Hence, the evaluation of these two expressions is quite straightforward, with the result

$$s_{21} = (\bar{a}^2/2)mm^{*-\frac{1}{2}}(m+m^*)^2(2\pi\beta)^{-5/2}\times\{g_{3/2}(z)\}^2\{g_{1/2}(z^*)-g_{3/2}(z^*)\}, \quad (54)$$

and

$$s_{22} = (\bar{a}^2/2)m^{-1/2}m^*(m+m^*)^2(2\pi\beta)^{-5/2}\times\{g_{1/2}(z)-g_{3/2}(z)\}\{g_{3/2}(z^*)\}^2. \quad (55)$$

In the case of (53) one needs the off-diagonal elements of $u_{11}$, which also are easily obtainable from (29). The expression then takes the form

$$s_{23} = \frac{\bar{a}^2}{256\pi^7\mu^2}\int\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)\mathfrak{M}(2^*)$$
$$\times\exp\{-\beta[E(1)+E(2)+E(1^*)+E(2^*)]\}$$
$$\times\Delta^{-2}(e^{\beta\Delta}+e^{-\beta\Delta}-2)\delta^3(1+1^*-2-2^*), \quad (56)$$

where

$$\Delta = E(1)+E(1^*)-E(2)-E(2^*). \quad (57)$$

Explicit evaluation of (56), added to some other integrals obtained later, is done in the Appendix.

III. We now consider the third sum in (41). About the $\delta^3$ functions, we have here the same situation as in the case of the second sum. However, the fourfold integration that is left after the various $\delta^3$ functions (except the one still associated with the product $U_{20}U_{11}$) are properly utilized, has three unstarred variables and one starred. The choice of three variables 1, 2, 3 out of the total number $l$ can be made in $l(l-1)(l-2)/6$ ways and that of one variable $1^*$ out of the total number $l^*$ in $l^*$ ways. Further, the remaining $(l-3)$ unstarred variables would be mutually permuted (in the bras of the factors $U_{10}$) in $(l-3)!$ ways, while the remaining $(l^*-1)$ starred variables (in the bras of the factors $U_{01}$) in $(l^*-1)!$ ways. Finally, it is not difficult to see that having made the choice of 1, 2, 3, and $1^*$, there are 12 ways of constructing the product $U_{20}U_{11}$. Hence, the contribution from the third sum to the coefficient $b_{ll^*}{}^q$

would be

$$2(8\pi^3)^{-1}\sum_{n_1,n_2,n_3}\int\langle 2,3|u_{20}|1,3\rangle\langle 1,1^*|u_{11}|2,1^*\rangle\delta^3(1-2)\exp\{-\beta[n_1E(1)+n_2E(2)+n_3E(3)+(l^*-1)E(1^*)]\},\quad(58)$$

where the summation extends over all integers $n_1$, $n_2$, $n_3\geqslant 0$, satisfying the condition $n_1+n_2+n_3=l-3$. The contribution to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ is, therefore,

$$s_3=(4\pi^3)^{-1}\int\langle 1,3|u_{20}|1,3\rangle\langle 1,1^*|u_{11}|1,1^*\rangle\{\mathfrak{M}(1)\}^2\mathfrak{M}(3)\mathfrak{M}(1^*)$$
$$=4a\bar{a}mm^{*1/2}(m+m^*)(2\pi\beta)^{-5/2}[g_{1/2}(z)-g_{3/2}(z)]g_{3/2}(z)g_{3/2}(z^*).\quad(59)$$

IV. One calculates the contribution from the fourth sum in (41) in the same manner as in the case of the third sum. The result comes out to be

$$s_4=4a^*\bar{a}m^{1/2}m^*(m+m^*)(2\pi\beta)^{-5/2}g_{3/2}(z)[g_{1/2}(z^*)-g_{3/2}(z^*)]g_{3/2}(z^*).\quad(60)$$

V. In order to evaluate the fifth sum in (41) we have first of all to determine the momentum representation of $U_{21}$. To second order, this is given by the first six terms of the expansion (28). These terms are in one-to-one correspondence with the first six diagrams for the representation of $U_{30}$ given in Fig. 5 of LYI.[4] To adapt those diagrams to the case of $U_{21}$, one has just to replace their coordinates $3'$ and 3 by $1^{*\prime}$ and $1^*$, respectively. Examining the six terms (or diagrams) one by one, we find that for the first four in which the starred variable appears only in one of the two $B$'s,

$$\langle 1,2,1^*|u_{21}|1,2,1^*\rangle=\langle 2,1,1^*|u_{21}|1,2,1^*\rangle=\frac{a\bar{a}\beta^2}{16\pi^4\mu m}\exp\{-\beta[E(1)+E(2)+E(1^*)]\},\quad(61)$$

while for the fifth or the sixth, in which case the starred variable appears in both the $B$'s,

$$\langle 1,2,1^*|u_{21}|1,2,1^*\rangle=\frac{\bar{a}^2}{32\pi^4\mu^2}\beta^2\exp\{-\beta[E(1)+E(2)+E(1^*)]\},\quad(62)$$

whereas

$$\langle 2,1,1^*|u_{21}|1,2,1^*\rangle=\frac{\bar{a}^2}{16\pi^4\mu^2}\exp\{-\beta[E(1)+E(2)+E(1^*)]\}\times\Delta'^{-2}(e^{\beta\Delta'}-\beta\Delta'-1),\quad(63)$$

with

$$\Delta'=E(1^*)+E(2)-E(1)-E((1^*+2-1)^*).\quad(64)$$

Respective contributions to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ from the terms of the types displayed in (61), (62), and (63) would be given by

$$s_5=s_{51}+s_{52}+s_{53},\quad(65)$$

where

$$s_{51}=4(8\pi^3)^{-1}\frac{a\bar{a}\beta^2}{16\pi^4\mu m}\int\exp\{-\beta[E(1)+E(2)+E(1^*)]\}\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)$$
$$=4a\bar{a}mm^{*1/2}(m+m^*)(2\pi\beta)^{-5/2}\{g_{3/2}(z)\}^2g_{3/2}(z^*),\quad(66)$$

$$s_{52}=(8\pi^3)^{-1}\frac{\bar{a}^2\beta^2}{32\pi^4\mu^2}\int\exp\{-\beta[E(1)+E(2)+E(1^*)]\}\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)$$
$$=(\bar{a}^2/2)mm^{*-1/2}(m+m^*)^2(2\pi\beta)^{-5/2}\{g_{3/2}(z)\}^2g_{3/2}(z^*),\quad(67)$$

and

$$s_{53}=\frac{\bar{a}^2}{128\pi^7\mu^2}\int\exp\{-\beta[E(1)+E(2)+E(1^*)]\}\mathfrak{M}(1)\mathfrak{M}(2)\mathfrak{M}(1^*)\Delta'^{-2}(e^{\beta\Delta'}-\beta\Delta'-1),\quad(68)$$

with $\Delta'$ as defined in (64).

VI. In order to evaluate the contribution to $\sum b_{ll^*}{}^q z^l z^{*l^*}$ from the sixth sum in (41) we proceed exactly in the same way as in the case of the fifth sum. The result is

$$s_6=s_{61}+s_{62}+s_{63},\quad(69)$$

where

$$s_{61}=4a^*\bar{a}m^{1/2}m^*(m+m^*)\times(2\pi\beta)^{-5/2}g_{3/2}(z)\{g_{3/2}(z^*)\}^2,\quad(70)$$

$$s_{62}=(\bar{a}^2/2)m^{-1/2}m^*(m+m^*)^2\times(2\pi\beta)^{-5/2}g_{3/2}(z)\{g_{3/2}(z^*)\}^2,\quad(71)$$

and

$$s_{63}=\frac{\bar{a}^2}{128\pi^7\mu^2}\int \exp\{-\beta[E(1)+E(1^*)+E(2^*)]\}\mathfrak{M}(1)\mathfrak{M}(1^*)\mathfrak{M}(2^*)\Delta''^{-2}(e^{\beta\Delta''}-\beta\Delta''-1), \tag{72}$$

with

$$\Delta''=E(1)+E(2^*)-E(1^*)-E((1+2^*-1^*)). \tag{73}$$

In the Appendix we have evaluated the integrals appearing in (68) and (72) added to the one appearing in (56). Combining the result thus obtained with the ones embodied in (49), (54), (55), (59), (60), (66), (67), (70), and (71), we finally obtain

$$\sum_{l,l^*=1}^{\infty} b_{ll^*}{}^q z^l z^{*l^*}=\sum_{\substack{i,j=1,2\\ i\neq j}}\{-\tfrac{1}{2}a_{ij}m_i^{1/2}m_j^{1/2}(m_i+m_j)(2\pi\beta)^{-2}g_{3/2}(z_i)g_{3/2}(z_j)$$
$$+4a_ia_{ij}m_im_j^{1/2}(m_i+m_j)(2\pi\beta)^{-5/2}g_{1/2}(z_i)g_{3/2}(z_i)g_{3/2}(z_j)$$
$$+\tfrac{1}{2}a_{ij}^2m_im_j^{-1/2}(m_i+m_j)^2(2\pi\beta)^{-5/2}[g_{3/2}(z_i)]^2g_{1/2}(z_j)$$
$$+2a_{ij}^2m_im_j^{1/2}(m_i+m_j)(2\pi\beta)^{-5/2}F_{ij}+\cdots\}, \tag{74}$$

where now

$$m_1\equiv m,\quad m_2\equiv m^*,\quad z_1\equiv z,\quad z_2\equiv z^*,$$
$$a_1\equiv a,\quad a_2\equiv a^*,\quad a_{ij}=a_{ji}\equiv\bar{a},$$

and

$$F_{ij}=\sum_{r,s,t=1}^{\infty}\frac{z_i^{r+s}z_j^t}{(rst)^{1/2}(r+s)}\,\frac{r+\zeta_{ij}s}{r(s+t)+\zeta_{ij}^2s(t-r)}, \tag{75}$$

with

$$\zeta_{ij}=(m_i-m_j)/(m_i+m_j).$$

Equations (36), (37), and (74), taken together, then give the full fugacity expansion for the system under consideration.

## 6. FUGACITY EXPANSION FOR A MULTICOMPONENT SYSTEM COMPOSED OF HARD-SPHERE SPINLESS BOSONS

Let us now consider the effect of introducing more components into the foregoing system. It is obvious that in the case of a three-component system the final result would consist of three "pure" parts like (36) or (37), three "mixed" ones like (74) and an *extra* one arising out of contributions from the second-order interactions in which *all* the three kinds of particles appear together.

Denoting the various quantities corresponding to the third component by symbols carrying a double asterisk (**), one readily sees that the additional second-order terms in the expansion of the quantum-statistical function $U_{ll^*l^{**}}{}^q$ in terms of the Boltzmannian functions $U_{nn^*n^{**}}$ would be (for all the three indices of symmetry being equal to $+1$)

$$\begin{aligned}&\sum\{U_{100}\cdots U_{100}\}\{U_{110}\}\{U_{101}\}\{U_{010}\cdots U_{010}\}\{U_{001}\cdots U_{001}\}\\&+\sum\{U_{100}\cdots U_{100}\}\{U_{110}\}\{U_{010}\cdots U_{010}\}\{U_{011}\}\{U_{001}\cdots U_{001}\}\\&+\sum\{U_{100}\cdots U_{100}\}\{U_{101}\}\{U_{010}\cdots U_{010}\}\{U_{011}\}\{U_{001}\cdots U_{001}\}\\&+\sum\{U_{100}\cdots U_{100}\}\{U_{111}\}\{U_{010}\cdots U_{010}\}\{U_{001}\cdots U_{001}\};\end{aligned} \tag{76}$$

the summations are to be carried over all *permissible* permutations (in the sense of the rule relevant to a tertiary mixture) of the variables appearing in the bras of the matrix elements of the various factors here.

We now evaluate, one by one, the contributions to

$$\sum_{l,l^*,l^{**}=1}^{\infty} b_{ll^*l^{**}}{}^q z^l z^{*l^*} z^{**l^{**}} \tag{77}$$

from the various sums in (76). Let us first consider a typical term in the first sum

$$\{U_{100}\cdots U_{100}\}\langle i',i^{*\prime}|U_{110}|1,1^*\rangle\langle j',i^{**\prime}|U_{101}|2,1^{**}\rangle\times\{U_{010}\cdots U_{010}\}\{U_{001}\cdots U_{001}\}. \tag{78}$$

In order to compute its contribution to the subsidiary operator $u_{ll^*l^{**}}{}^q$, we notice that (78) contains in all $(l+l^*+l^{**}-2)$ $\delta^3$ functions. One $\delta^3$ function, belonging either to the factor $U_{110}$ or $U_{101}$, can be written (with the help of the other $\delta^3$ functions) as

$$\delta^3\{\sum_{\alpha,\alpha^*,\alpha^{**}}(\mathbf{k}_\alpha'+\mathbf{k}_{\alpha^*}'+\mathbf{k}_{\alpha^{**}}')-\sum_{\alpha,\alpha^*,\alpha^{**}}(\mathbf{k}_\alpha+\mathbf{k}_{\alpha^*}+\mathbf{k}_{\alpha^{**}})\} \tag{79}$$

and dropped in going from $U_{ll^*l^{**}}{}^q$ to $u_{ll^*l^{**}}{}^q$. We are then left with $(l+l^*+l^{**}-4)$ $\delta^3$ functions associated with the factors $U_{100}$, $U_{010}$, and $U_{001}$ and one $\delta^3$ function with the remaining factor. Consequently, for the determination of the contribution of this particular term to the fugacity coefficient $b_{ll^*l^{**}}{}^q$, $(l+l^*+l^{**}-4)$ integrations can be carried out straightaway, leaving thereby an integral over the remaining four momentum variables **1**, **2**, **1***, and **1****, with the integrand still containing one $\delta^3$ function. It is not difficult to see that the contribution from the first sum in (76) to $b_{ll^*l^{**}}{}^q$ would be

$$(8\pi^3)^{-1}\sum_{n_1,n_2}\int\langle \mathbf{2},\mathbf{1}^*|u_{110}|\mathbf{1},\mathbf{1}^*\rangle\langle\mathbf{1},\mathbf{1}^{**}|u_{101}|\mathbf{2},\mathbf{1}^{**}\rangle\delta^3(\mathbf{1}-\mathbf{2})\times\exp\{-\beta[n_1E(\mathbf{1})+n_2E(\mathbf{2})+(l^*-1)E(\mathbf{1}^*)+(l^{**}-1)E(\mathbf{1}^{**})]\},\quad(80)$$

the summation extending over all integers $n_1$, $n_2\geqslant 0$, satisfying the condition $n_1+n_2=l-2$. The contribution to the series expansion (77) is, therefore,

$$s_7=(8\pi^3)^{-1}\int\langle\mathbf{1},\mathbf{1}^*|u_{110}|\mathbf{1},\mathbf{1}^*\rangle\langle\mathbf{1},\mathbf{1}^{**}|u_{101}|\mathbf{1},\mathbf{1}^{**}\rangle\{\mathfrak{M}(\mathbf{1})\}^2\mathfrak{M}(\mathbf{1}^*)\mathfrak{M}(\mathbf{1}^{**}),\quad(81)$$

where the $\mathfrak{M}$ functions are defined by (46), (47), and another similar equation for the particles of the third kind. For the diagonal elements of $u_{110}$ and $u_{101}$ we have expressions similar to the one given earlier for the function $u_{11}$; we have only to substitute the proper "reduced mass" and the proper "hard-sphere diameter" for the quantities $\mu$ and $\bar{a}$. Equation (81) then gives

$$s_7=\frac{a_{12}a_{13}\beta^2}{128\pi^7\mu_{12}\mu_{13}}\int\exp\{-\beta[2E(\mathbf{1})+E(\mathbf{1}^*)+E(\mathbf{1}^{**})]\}\{\mathfrak{M}(\mathbf{1})\}^2\mathfrak{M}(\mathbf{1}^*)\mathfrak{M}(\mathbf{1}^{**})$$
$$=a_{12}a_{13}m^{-1/2}m^{*1/2}m^{**1/2}(m+m^*)(m+m^{**})(2\pi\beta)^{-5/2}\{g_{1/2}(z)-g_{3/2}(z)\}g_{3/2}(z^*)g_{3/2}(z^{**}).\quad(82)$$

Corresponding contributions from the second and the third sums in (76) would obviously be

$$s_8=a_{12}a_{23}m^{1/2}m^{*-1/2}m^{**1/2}(m+m^*)(m^*+m^{**})(2\pi\beta)^{-5/2}g_{3/2}(z)[g_{1/2}(z^*)-g_{3/2}(z^*)]g_{3/2}(z^{**}),\quad(83)$$

and

$$s_9=a_{13}a_{23}m^{1/2}m^{*1/2}m^{**-1/2}(m+m^{**})(m^*+m^{**})(2\pi\beta)^{-5/2}g_{3/2}(z)g_{3/2}(z^*)[g_{1/2}(z^{**})-g_{3/2}(z^{**})],\quad(84)$$

respectively.

We now consider the fourth sum in (76). The momentum representation of $U_{111}$ can easily be obtained by considering its expansion in terms of the various binary kernels. One thereby gets for the subsidiary operator

$$\langle\mathbf{1},\mathbf{1}^*,\mathbf{1}^{**}|u_{111}|\mathbf{1},\mathbf{1}^*,\mathbf{1}^{**}\rangle=\left(\frac{a_{12}a_{23}}{\mu_{12}\mu_{23}}+\frac{a_{13}a_{23}}{\mu_{13}\mu_{23}}+\frac{a_{12}a_{13}}{\mu_{12}\mu_{13}}\right)\frac{\beta^2}{16\pi^4}\exp\{-\beta[E(\mathbf{1})+E(\mathbf{1}^*)+E(\mathbf{1}^{**})]\},\quad(85)$$

correct to the second order. The corresponding contribution to the series (77) would be

$$s_{10}=\left(\frac{a_{12}a_{23}}{\mu_{12}\mu_{23}}+\frac{a_{13}a_{23}}{\mu_{13}\mu_{23}}+\frac{a_{12}a_{13}}{\mu_{12}\mu_{13}}\right)\frac{\beta^2}{128\pi^7}\int\exp\{-\beta[E(\mathbf{1})+E(\mathbf{1}^*)+E(\mathbf{1}^{**})]\}\mathfrak{M}(\mathbf{1})\mathfrak{M}(\mathbf{1}^*)\mathfrak{M}(\mathbf{1}^{**})$$
$$=\left(\frac{a_{12}a_{23}}{\mu_{12}\mu_{23}}+\frac{a_{13}a_{23}}{\mu_{13}\mu_{23}}+\frac{a_{12}a_{13}}{\mu_{12}\mu_{13}}\right)(mm^*m^{**})^{3/2}(2\pi\beta)^{-5/2}g_{3/2}(z)g_{3/2}(z^*)g_{3/2}(z^{**}).\quad(86)$$

Combining (82), (83), (84), and (86), one gets

$$\tfrac{1}{2}(2\pi\beta)^{-5/2}\sum_{\substack{i,j,k=1\\ i\neq j\neq k}}^{3}a_{ij}a_{jk}m_i^{1/2}m_j^{-1/2}m_k^{1/2}(m_i+m_j)(m_j+m_k)g_{3/2}(z_i)g_{1/2}(z_j)g_{3/2}(z_k)\quad(87)$$

as the total contribution to the fugacity expansion of the system from the mutual interactions among *all* the three kinds of particles present.

The full fugacity expansion in the case of a multicomponent system, correct to the second order in the interaction parameters, can now be written down directly because it is quite straightforward to see that, up to the order considered here, an addition of further components to the tertiary system would not give rise to any *new* type of terms except the ones already considered, but with the suffices permuted among the various components. However, before we write down the final result, we will generalize our treatment to the case of particles obeying arbitrary statistics and having arbitrary spin values.

## 7. PARTICLES WITH ARBITRARY SPIN AND STATISTICS

The treatment given in the preceding sections can be readily generalized to the case where the particles constituting the system have arbitrary spin values. While considering this generalization one must naturally keep in mind the statistics governing the various components. Now, since the $z$ component of the particle spin is conserved, just as the momentum components are, the foregoing formalism requires only very formal alterations, e.g., the arguments of the various state vectors must now include the spin coordinates along with the momenta and consequently, the integrations (over the various momenta) must be augmented by the summations (over the various spin coordinates). Next, because of the fact that the hard-sphere interaction is spin independent these alterations do not modify the previous results in any manner other than the introduction of certain new factors depending exclusively on the spins, and on the statistics, of the particles. In order to determine these factors we proceed exactly in the manner of Lee and Yang[4] (see LYII); in practice, however, one may make use of the following working rule:

Take any particular contribution (to the fugacity series), written after all the elementary integrations have been carried out to yield factors of the type $\mathfrak{M}(\mathbf{k}_i)$ and consider the group of variables appearing in the bras of the various matrix elements, which are yet present in the integrand, as a permutation of the variables appearing in the kets. One thus finds different permutation subgroups which are concerned with *mutually exclusive* variables. Write, for each of these subgroups the factor $(2J_i+1)$ where $J_i$ is the spin value of the particles (belonging, say, to the $i$th component) with which this particular subgroup is concerned.[11] Next, for each of these subgroups, write the factor $\gamma_i^{(P)}$ where $\gamma_i$ is the index of symmetry of the $i$th component and $(P)$ is the order of the permutation involved. Finally, replace the factors $\mathfrak{M}(\mathbf{k}_i)$ in the integrand by the generalized factors $\mathfrak{M}'(\mathbf{k}_i)$, where

$$\mathfrak{M}'(\mathbf{k}_i)=z_i\{1-\gamma_i z_i \exp[-\beta E(\mathbf{k}_i)]\}^{-1}, \tag{88}$$

or else replace, in the integrated result, the activity coefficients $z_i$ by $\gamma_i z_i$ and write for each of the factors $\mathfrak{M}(\mathbf{k}_i)$ an extra factor $\gamma_i$.

Incorporating all these changes with respect to all the components $i$, the final result would become appropriate to the generalized situation under consideration. It is not difficult to see that, in view of the aforelaid rule, the various results obtained above are modified in the following manner.[12]

We thus find that the contribution $s_1$ gets modified by the factor $(2J+1)(2J^*+1)\gamma\gamma^*$, $s_{21}$ by $(2J+1)^2\times(2J^*+1)\gamma^*$, $s_{22}$ by $(2J+1)(2J^*+1)^2\gamma$, and $s_{23}$ by $(2J+1)(2J^*+1)\gamma\gamma^*$. Next, one half of the contribution $s_3$ gets multiplied[13] by the factor $(2J+1)^2(2J^*+1)\gamma^*$ and the other half by $(2J+1)(2J^*+1)\gamma\gamma^*$; the weighted mean factor would thus be $\frac{1}{2}(2J+1)(2J+1+\gamma)\times(2J^*+1)\gamma^*$. Similarly, $s_4$ gets modified by the factor $\frac{1}{2}(2J+1)(2J^*+1)(2J^*+1+\gamma^*)\gamma$. Next, we come to the contributions $s_5$ and $s_6$. Here we find for $s_{51}$ the weighted mean factor

$$\tfrac{1}{2}[(2J+1)^2(2J^*+1)\gamma^*+(2J+1)(2J^*+1)\gamma\gamma^*] =\tfrac{1}{2}(2J+1)(2J+1+\gamma)(2J^*+1)\gamma^*$$

and similarly for $s_{61}$ the factor

$$\tfrac{1}{2}(2J+1)(2J^*+1)(2J^*+1+\gamma^*)\gamma.$$

The relevant factors for $s_{52}$ and $s_{62}$ will be $(2J+1)^2\times(2J^*+1)\gamma^*$ and $(2J+1)(2J^*+1)^2\gamma$, respectively, while for both $s_{53}$ and $s_{63}$ we shall have $(2J+1)\times(2J^*+1)\gamma\gamma^*$.

Let us now consider the modification of the various contributions evaluated in the preceding section. Referring to (80) and (81), one notes that the relevant factor for the contribution $s_7$ would be $(2J+1)\times(2J^*+1)(2J^{**}+1)\gamma\gamma^*\gamma^{**}$. By symmetry, this very factor will go with the contributions $s_8$ and $s_9$. Further, one finds from (85) and (86) that $s_{10}$ will also get multiplied by the same factor—and so will the final result (87).

We are now in a position to write down the final, second-order, expression for the fugacity expansion of a quantum-mechanical system with $\nu$ components. Combining the various results obtained above, we finally get

$$\sum_{\substack{\{l_\sigma\}=0\\ \Sigma_\sigma l_\sigma\geq 1}}^{\infty} b_{\{l_\sigma\}}{}^q z_1{}^{l_1}\cdots z_\nu{}^{l_\nu}$$

$$=\sum_{i=1}^{\nu}(m_i/2\pi\beta)^{3/2}(2J_i+1)\gamma_i[g_{5/2}(\gamma_i z_i)-a_i(m_i/2\pi\beta)^{1/2}(2J_i+1+\gamma_i)\gamma_i\{g_{3/2}(\gamma_i z_i)\}^2$$
$$+2a_i^2(m_i/2\pi\beta)(2J_i+1+\gamma_i)^2 g_{1/2}(\gamma_i z_i)\{g_{3/2}(\gamma_i z_i)\}^2+4a_i^2(m_i/2\pi\beta)(2J_i+1+\gamma_i)\gamma_i F_i+\cdots]$$

[11] It may be noted that the various contributions, as written in the foregoing, have first to be split into certain, physically distinct, subcontributions before the above-mentioned factors are assigned. For $J=0$, this splitting was not necessary.

[12] For the "pure" parts, the relevant factors have already been determined in LYII.

[13] Refer to (58), (59), and footnote 11.

$$+\sum_{\substack{i,j=1\\i\neq j}}^{\nu}\left[\frac{m_im_j(m_i+m_j)}{(2\pi\beta)^3}\right]^{1/2}(2J_i+1)(2J_j+1)\gamma_i\gamma_ja_{ij}\left\{-\frac{1}{2}\left(\frac{m_i+m_j}{2\pi\beta}\right)^{1/2}g_{3/2}(\gamma_iz_i)g_{3/2}(\gamma_jz_j)+2a_i\left[\frac{m_i(m_i+m_j)}{(2\pi\beta)^2}\right]^{1/2}\right.$$

$$\times(2J_i+1+\gamma_i)\gamma_ig_{1/2}(\gamma_iz_i)g_{3/2}(\gamma_iz_i)g_{3/2}(\gamma_jz_j)+\tfrac{1}{2}a_{ij}\left[\frac{m_i(m_i+m_j)^3}{m_j^2(2\pi\beta)^2}\right]^{1/2}(2J_i+1)\gamma_i\{g_{3/2}(\gamma_iz_i)\}^2g_{1/2}(\gamma_jz_j)$$

$$\left.+2a_{ij}\left[\frac{m_i(m_i+m_j)}{(2\pi\beta)^2}\right]^{1/2}F_{ij}+\cdots\right\}$$

$$+\sum_{\substack{i,j,k=1\\i\neq j\neq k}}^{\nu}\frac{1}{2}\left[\frac{m_im_jm_k}{(2\pi\beta)^3}\right]^{1/2}(2J_i+1)(2J_j+1)(2J_k+1)\gamma_i\gamma_j\gamma_k$$

$$\times\frac{(m_i+m_j)(m_j+m_k)}{(2\pi\beta)m_j}a_{ij}a_{jk}g_{3/2}(\gamma_iz_i)g_{1/2}(\gamma_jz_j)g_{3/2}(\gamma_kz_k)+\cdots,\quad(89)$$

where the symbol $\{l_\sigma\}$ stands for the totality of the numbers $l_1,\cdots l_\nu$ and the free indices $i$, $j$, and $k$ on the right-hand side refer to the various components in the system. The algebraic functions appearing in the foregoing expression are defined as follows:

$$g_n(\gamma_iz_i)=\sum_{l=1}^{\infty}l^{-n}(\gamma_iz_i)^l,\quad(90)$$

$$F_i=\sum_{r,s,t=1}^{\infty}(rst)^{-1/2}(r+s)^{-1}(s+t)^{-1}(\gamma_iz_i)^{r+s+t},\quad(91)$$

and

$$F_{ij}=\sum_{r,s,t=1}^{\infty}(rst)^{-1/2}(r+s)^{-1}(\gamma_iz_i)^{r+s}(\gamma_jz_j)^t\times\frac{r+\zeta_{ij}s}{r(s+t)+\zeta_{ij}^2s(t-r)},\quad(92)$$

with

$$\zeta_{ij}=(m_i-m_j)/(m_i+m_j).$$

The other quantities appearing here have their usual meaning; in particular, $a_{ij}$ is the hard-sphere diameter for mutual interaction between a particle of the $i$th kind and a particle of the $j$th kind. Moreover, by notation, $a_i\equiv a_{ii}$.

### 8. THE VIRIAL COEFFICIENTS

Having obtained an explicit expression for the fugacity expansion of the system under investigation, we can now readily evaluate the various virial coefficients. For this purpose, we first note that the equation of state of this (infinitely large) system would be given by

$$p/kT=\sum_{\substack{\{l_\sigma\}=0\\\Sigma_\sigma l_\sigma\geq1}}^{\infty}b_{\{l_\sigma\}}{}^qz_1^{l_1}\cdots z_\nu^{l_\nu},\quad(93)$$

along with the following set of $\nu$ equations for the (partial) particle densities:

$$\rho_\sigma=\sum_{\substack{\{l_\sigma\}=0\\\Sigma_\sigma l_\sigma\geq1}}^{\infty}l_\sigma b_{\{l_\sigma\}}{}^qz_1^{l_1}\cdots z_\nu^{l_\nu};\sigma=1,2,\cdots\nu,\quad(94)$$

One can eliminate from the $(\nu+1)$ equations (93) and (94) the $\nu$ quantities $z_1,\cdots z_\nu$ and obtain thereby a polynomial expansion for $p/kT$ in terms of the quantities $\rho_1,\cdots\rho_\nu$. The resulting polynomial can then be compared with the virial expansion

$$p/kT=\sum_{i=1}^{\nu}\rho_i+\sum_{i,j=1}^{\nu}B_{ij}\rho_i\rho_j+\sum_{i,j,k=1}^{\nu}C_{ijk}\rho_i\rho_j\rho_k+\cdots,\quad(95)$$

which, in view of the form of our result (89), may be rewritten as

$$p/kT=\sum_{i=1}^{\nu}[\rho_i+B_{ii}\rho_i^2+C_{iii}\rho_i^3+\cdots]+\sum_{\substack{i,j=1\\i\neq j}}^{\nu}[B_{ij}\rho_i\rho_j+3C_{iij}\rho_i^2\rho_j+\cdots]+\sum_{\substack{i,j,k=1\\i\neq j\neq k}}^{\nu}[C_{ijk}\rho_i\rho_j\rho_k+\cdots]+\cdots.\quad(96)$$

A little algebra gives the following relations between the virial coefficients and the fugacity coefficients[14]:

$$B_{ii}=-(b_{l_i=1}{}^q)^{-2}b_{l_i=2}{}^q,\quad(97)$$

$$B_{ij}=-\tfrac{1}{2}(b_{l_i=1}{}^qb_{l_j=1}{}^q)^{-1}b_{l_{i,j}=1}{}^q,\quad(98)$$

$$C_{iii}=(b_{l_i=1}{}^q)^{-4}[4(b_{l_i=2}{}^q)^2-2b_{l_i=3}{}^qb_{l_i=1}{}^q],\quad(99)$$

$$C_{iij}=\tfrac{1}{3}(b_{l_i=1}{}^qb_{l_j=1}{}^q)^{-2}\times[(b_{l_{i,j}=1}{}^q)^2+4b_{l_i=2}{}^qb_{l_{i,j}=1}{}^qb_{l_j=1}{}^q(b_{l_i=1}{}^q)^{-1}-2b_{l_i=2,l_j=1}{}^qb_{l_j=1}{}^q],\quad(100)$$

and

$$C_{ijk}=\tfrac{1}{3}(b_{l_i=1}{}^qb_{l_j=1}{}^qb_{l_k=1}{}^q)^{-1}\times[b_{l_{i,j}=1}{}^qb_{l_{i,k}=1}{}^q(b_{l_i=1}{}^q)^{-1}+b_{l_{i,j}=1}{}^qb_{l_{j,k}=1}{}^q(b_{l_j=1}{}^q)^{-1}+b_{l_{i,k}=1}{}^qb_{l_{j,k}=1}{}^q(b_{l_k=1}{}^q)^{-1}-b_{l_{i,j,k}=1}{}^q].\quad(101)$$

[14] To avoid complicated suffices for the specific $b_{\{l_\sigma\}}{}^q$'s we exclude from the set $\{l_\sigma\}$ the mention of all those $l$'s which are equal to zero.

The various coefficients appearing on the right-hand sides of these relations can be readily obtained from (89) by expanding the algebraic functions there as power series in the activities $z_i$; this is so because the region of interest in connection with the study of the virial coefficients is obviously the nondegenerate one, for which all $z_i \ll 1$. After some calculation, one obtains for the virial coefficients the following expressions:

$$B_{ii}=(2J_i+1)^{-1}(2\pi\beta/m_i)^{3/2}\times[-2^{-5/2}\gamma_i+(2J_i+1+\gamma_i)a_i(m_i/2\pi\beta)^{1/2}], \quad (102)$$

$$B_{ij}=\tfrac{1}{2}a_{ij}(2\pi\beta)(m_i+m_j)/m_im_j, \quad (103)$$

$$C_{iii}=(2J_i+1)^{-2}(2\pi\beta/m_i)^3[(1/8-2/3^{5/2})-2\gamma_i(2J_i+1+\gamma_i)a_i^2(m_i/2\pi\beta)], \quad (104)$$

$$C_{iij}=-\tfrac{2}{3}a_{ij}^2\gamma_i(2J_i+1)^{-1}(2\pi\beta/m_i)(2\pi\beta/m_j), \quad (105)$$

and

$$C_{ijk}=0, \quad (106)$$

correct to the second order in the interaction parameters.

We note that the "pure" virial coefficients, $B_{ii}$ and $C_{iii}$, are exactly the same as one obtains in the case of a single-component system[15]; this is, of course, as expected. The influence of the mutual interactions between particles of different kinds shows itself in the "mixed" virial coefficients. The lowest "mixed" coefficient, $B_{ij}$, which is found to be of the first order of magnitude, is completely independent of the spin and statistics of the particles involved; it rather depends only on the relevant interaction parameter and the thermal wavelength corresponding to the respective "reduced" mass. In the language of de Boer,[16] one can say that this particular virial coefficient represents only the *diffraction* effects of quantum mechanics and not the *symmetry* effects of quantum statistics.

The "mixed" coefficient of the next higher order, $C_{iij}$, is only of the second order, its magnitude depending, apart from the mutual interaction parameter, on the two individual thermal wavelengths (which contribute equally to the diffraction effects) and also on the spin and statistics of the dominating component (which obviously contribute to the symmetry effects).

Next, the coefficient $C_{ijk}$ is found to vanish so far as the order of our calculation goes.

At this stage, it appears worthwhile to mention that the results of the present investigation should be capable of generalization to the case of systems with interactions more realistic than the simple hard-sphere interactions considered here. This generalization, however, would be quite straightforward provided that the actual potentials are such that they do not lead to the formation of two-body bound states but at the same time the relative kinetic energy of the motion of two particles is much smaller than the attractive potential energy between them. These two conditions, a moment's reflection will show, are quite compatible with each other. Under these circumstances the only modification one expects in the foregoing results would consist in replacing everywhere the hard-sphere diameters by the respective scattering lengths

$$a'=-\lim_{k\to 0}[\eta_0(k)/k], \quad (107)$$

where $\eta_0(k)$ are the relevant phase shifts, corresponding to the two-body $S$ state, for the potentials involved.[17]

## 9. BOSE-EINSTEIN CONDENSATION IN A BINARY MIXTURE OF BOSONS AND FERMIONS

In this section we consider the statistical behavior of a two-component mixture, one component consisting of bosons and the other of fermions, as we approach (from above) the region of the so-called Bose-Einstein phase transition. Of immediate interest in this connection is the determination of the effect of particle interactions on the values of the various parameters that characterize the onset of this transition. It is easy to see that the foregoing formulation is not suited to treat this particular phenomenon successfully because of the fact that the function $\mathfrak{M}(\mathbf{k})$ for the boson component exhibits a singularity at $\mathbf{k}=0$ as the corresponding $z$ approaches unity. One therefore gets unnecessary infinities in the expressions for the various physical properties; however, these infinities, as has been shown by Lee and Yang[5] in the case of a pure Bose gas (LYIV), are only artificial and can actually be circumvented by reformulating the theory in terms of average occupation numbers in momentum space. The phase transition is then characterized by the appearance of a "singularity" in the ground-state occupation number of the system (assumed to be of an infinite extent).

Adopting the procedure laid down in LYIV, we define for the system under discussion the average occupation numbers for two components as follows:

Bose (unstarred):

$$\langle n_{\mathbf{k}}\rangle=\sum_{l=1}^{\infty}\sum_{l^*=0}^{\infty}\frac{z^l z^{*l^*}}{(l-1)!\,l^*!}\sum{}'\langle\mathbf{k}_1,\cdots\mathbf{k}_{l-1},\mathbf{k};\mathbf{k}_{1^*},\cdots\mathbf{k}_{l^*}|U_{ll^*}{}^q|\mathbf{k}_1,\cdots\mathbf{k}_{l-1},\mathbf{k};\mathbf{k}_{1^*},\cdots\mathbf{k}_{l^*}\rangle; \quad (108)$$

Fermi (starred):

$$\langle n_{\mathbf{k}^*}\rangle=\sum_{l=0}^{\infty}\sum_{l^*=1}^{\infty}\frac{z^l z^{*l^*}}{l!\,(l^*-1)!}\sum{}'\langle\mathbf{k}_1,\cdots\mathbf{k}_l;\mathbf{k}_{1^*},\cdots\mathbf{k}_{l^*-1},\mathbf{k}^*|U_{ll^*}{}^q|\mathbf{k}_1,\cdots\mathbf{k}_l;\mathbf{k}_{1^*},\cdots\mathbf{k}_{l^*-1},\mathbf{k}^*\rangle; \quad (109)$$

[15] See, e.g., A. Pais and G. E. Uhlenbeck, Phys. Rev. **116**, 250 (1959).

[16] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 6.

[17] This statement is made in view of the results of an earlier investigation into a single-component system; R. K. Pathria and M. P. Kawatra, Progr. Theoret. Phys. (Kyoto) **27**, 1085 (1962).

the primed summation in each of these two equations goes over all momenta except the one appearing on the left. As they must, the occupation numbers satisfy the following relations involving the grand partition function (G.P.F.):

$$\sum_{\mathbf{k}}\langle n_{\mathbf{k}}\rangle = z\frac{\partial}{\partial z}\ln(\text{G.P.F.}) = \Omega\rho, \tag{110}$$

$$\sum_{\mathbf{k}^*}\langle n_{\mathbf{k}^*}\rangle = z^*\frac{\partial}{\partial z^*}\ln(\text{G.P.F.}) = \Omega\rho^*, \tag{111}$$

with

$$\ln(\text{G.P.F.}) = \sum_{\substack{l,\,l^*=0\\(l+l^*)\geq 1}}^{\infty}\frac{z^l z^{*l^*}}{l!l^*!}\operatorname{Tr}(U_{ll^*}{}^q). \tag{112}$$

Introducing the functions

$$M(\mathbf{k}) = z[1+\langle n_{\mathbf{k}}\rangle], \tag{113}$$

and

$$M(\mathbf{k}^*) = z^*\{1-\langle n_{\mathbf{k}^*}\rangle\}, \tag{114}$$

the whole formulation can be recast in terms of these functions instead of the earlier ones. The phase transition would then occur at that value of $z(=z_c)$ where the boson function $M(0)$ becomes singular. In order to determine the critical value $z_c$, to the first order in the interaction parameters, we make use of the following relation, which can be shown to hold between the $\mathfrak{M}$ and $M$ functions:

$$\begin{aligned}\{\mathfrak{M}(\mathbf{k})\}^{-1}-\{M(\mathbf{k})\}^{-1} &= \sum_{\mathbf{k}_1} M(\mathbf{k})\{\langle\mathbf{k},\mathbf{k}_1|U_{20}|\mathbf{k},\mathbf{k}_1\rangle+\langle\mathbf{k}_1,\mathbf{k}|U_{20}|\mathbf{k},\mathbf{k}_1\rangle\}\\ &\quad+\sum_{\mathbf{k}_1^*} M(\mathbf{k}_{1^*})\langle\mathbf{k},\mathbf{k}_{1^*}|U_{11}|\mathbf{k},\mathbf{k}_{1^*}\rangle\\ &\quad+\text{terms of higher orders.}\end{aligned} \tag{115}$$

For a first-order calculation of the left-hand side here, one may substitute in the leading terms of the perturbation expansion on the right-hand side the ideal gas result $M=\mathfrak{M}$. Considering the state $\mathbf{k}=0$ and the situation corresponding to the approach of the transition point $\{M(0)=O(N)\}$, we obtain for $z_c$

$$\begin{aligned}z_c^{-1}-1 &= -4(2J+1)(J+1)(a/\lambda)\rho\lambda^3\\ &\quad-(2J+1)(2J^*+1)(\bar{a}/\bar{\lambda})\rho^*\bar{\lambda}^3+\cdots,\end{aligned} \tag{116}$$

where $\bar{\lambda}$ is the thermal wavelength corresponding to the reduced mass. For $J=0$ and $J^*=1/2$, corresponding to the physical case of a $He^4-He^3$ mixture, we get

$$z_c = 1+4(a/\lambda)\rho\lambda^3+2(\bar{a}/\bar{\lambda})\rho^*\bar{\lambda}^3+\cdots. \tag{117}$$

It may, however, be noted that at the transition point

$$\rho\lambda^3 = 2.612+\cdots. \tag{118}$$

On the other hand, for the Fermi part we have the result

$$\rho^*\lambda^{*3} = -2g_{3/2}(-z^*)+\cdots. \tag{119}$$

One can then readily write down for the equilibrium pressure of the system at the transition point

$$\begin{aligned}p_c/kT &= \{1.342\lambda^{-3}-2g_{5/2}(-z^*)\lambda^{*-3}\}\\ &\quad+\{2a\rho^2\lambda^2-2\bar{a}\rho\rho^*\bar{\lambda}^2+\tfrac{1}{2}a^*\rho^{*2}\lambda^{*2}\}+\cdots.\end{aligned} \tag{120}$$

One can then obtain the corresponding expressions for the various other physical quantities also.

In order to make a complete study of the influence of the particle interactions on the low-temperature behavior of the system, it is obviously necessary to extend the foregoing investigation to temperatures below the transition point. For this purpose, however, one has to consider in detail the generalization of the so-called $x$ ensemble introduced by Lee and Yang.[18] Study in this direction is in progress.

## APPENDIX

We evaluate here the integrals appearing in (56), (68), and (72) of the text. Since throughout the present investigation these integrals finally appear as a simple sum, they will not be considered here individually; rather we shall solve them together.

Let us first interchange the variables **1** and **2** in the integrand of (68) and then introduce therein the integral

$$\int\delta^3(\mathbf{1}+\mathbf{1}^*-\mathbf{2}-\mathbf{2}^*)d\mathbf{2}^*,$$

while $\Delta'$ (Eq. 64) is redefined as

$$\begin{aligned}\Delta' &= E(\mathbf{1}^*)+E(\mathbf{1})-E(\mathbf{2})-E(\mathbf{2}^*)\\ &\equiv\Delta.\end{aligned} \tag{121}$$

Next, let us interchange in the integrand of (72) the variables **1*** and **2*** and insert therein the integral

$$\int\delta^3(\mathbf{1}+\mathbf{1}^*-\mathbf{2}-\mathbf{2}^*)d\mathbf{2},$$

while $\Delta''$ (Eq. 73) is redefined as

$$\begin{aligned}\Delta'' &= E(\mathbf{1})+E(\mathbf{1}^*)-E(\mathbf{2}^*)-E(\mathbf{2})\\ &\equiv\Delta.\end{aligned} \tag{122}$$

Having done this the three integrals can be straightaway combined, with the result

$$\begin{aligned}I=\frac{\bar{a}^2}{128\pi^7\mu^2}\int &\exp\{-\beta[E(\mathbf{1})+E(\mathbf{2})+E(\mathbf{1}^*)+E(\mathbf{2}^*)]\}\delta^3(\mathbf{1}+\mathbf{1}^*-\mathbf{2}-\mathbf{2}^*)\mathfrak{M}(\mathbf{1})\mathfrak{M}(\mathbf{2})\mathfrak{M}(\mathbf{1}^*)\mathfrak{M}(\mathbf{2}^*)\Delta^{-2}\\ &\times\left[\tfrac{1}{2}(e^{\beta\Delta}+e^{-\beta\Delta}-2)+(e^{\beta\Delta}-\beta\Delta-1)\left(\frac{\exp[\beta E(\mathbf{2}^*)]}{\mathfrak{M}(\mathbf{2}^*)}+\frac{\exp[\beta E(\mathbf{2})]}{\mathfrak{M}(\mathbf{2})}\right)\right]d\mathbf{1}d\mathbf{2}d\mathbf{1}^*d\mathbf{2}^*,\end{aligned} \tag{123}$$

[18] T. D. Lee and C. N. Yang, Phys. Rev. **117**, 897 (1960).

where

$$\Delta=E(1)+E(1^*)-E(2)-E(2^*). \qquad (124)$$

Considering the factor inside the long bracket, viz.,

$$\Big[\tfrac{1}{2}(e^{\beta\Delta}+e^{-\beta\Delta}-2)-2(e^{\beta\Delta}-\beta\Delta-1)+(e^{\beta\Delta}-\beta\Delta-1)\Big(\frac{\exp[\beta E(2^*)]}{z^*}+\frac{\exp[\beta E(2)]}{z}\Big)\Big], \qquad (125)$$

we note that since the other factors in the integrand of (123) are invariant under the interchanges $1\leftrightarrow 2$, $1^*\leftrightarrow 2^*$ (which involve the transformation $\Delta\rightarrow -\Delta$), we may replace the middle term in (125) by

$$-\{(e^{\beta\Delta}-\beta\Delta-1)+(e^{-\beta\Delta}+\beta\Delta-1)\}=-(e^{\beta\Delta}+e^{-\beta\Delta}-2).$$

The expression (125) itself may therefore be replaced by

$$\Big[-\tfrac{1}{2}(e^{\beta\Delta}+e^{-\beta\Delta}-2)+(e^{\beta\Delta}-\beta\Delta-1)\times\Big(\frac{\exp[\beta E(2^*)]}{z^*}+\frac{\exp[\beta E(2)]}{z}\Big)\Big].$$

Now, proceeding along the sequence of steps similar to the ones indicated in LYII [Eqs. (74)-(77), etc.], we obtain

$$I=-\bar{a}^2mm^*(m+m^*)^2(2\pi\beta)^{-5/2}[\Sigma_0+\Sigma_1+\Sigma_2], \qquad (126)$$

where

$$\Sigma_0=\sum_{\substack{n_1,n_2,\\ n_3,n_4=1}}^{\infty}\frac{(\alpha_0+\beta_0+\gamma_0)^{1/2}-(\alpha_0)^{1/2}-\beta_0/2(\alpha_0)^{1/2}}{(\beta_0/2)^2-\alpha_0\gamma_0}z^{n_1+n_2}z^{*n_3+n_4}, \qquad (127)$$

$$\Sigma_1=\sum_{n_1,n_2,n_3=1}^{\infty}\frac{(\alpha_1+\beta_1+\gamma_1)^{1/2}-(\alpha_1)^{1/2}-\beta_1/2(\alpha_1)^{1/2}}{(\beta_1/2)^2-\alpha_1\gamma_1}z^{n_1+n_2}z^{*n_3}, \qquad (128)$$

$$\Sigma_2=\sum_{n_1,n_3,n_4=1}^{\infty}\frac{(\alpha_2+\beta_2+\gamma_2)^{1/2}-(\alpha_2)^{1/2}-\beta_2/2(\alpha_2)^{1/2}}{(\beta_2/2)^2-\alpha_2\gamma_2}z^{n_1}z^{*n_3+n_4}, \qquad (129)$$

$$\alpha_0=m(n_1n_3n_4+n_2n_3n_4)+m^*(n_1n_2n_3+n_1n_2n_4),$$
$$\beta_0=(m+m^*)(n_1n_3-n_2n_4)+(m-m^*)(n_2n_3-n_1n_4), \qquad (130)$$
$$\gamma_0=-m(n_1+n_2)-m^*(n_3+n_4),$$

while

$$(\alpha_1,\beta_1,\gamma_1)=(\alpha_0,\beta_0,\gamma_0)_{n_4=0}, \qquad (131)$$

and

$$(\alpha_2,\beta_2,\gamma_2)=(\alpha_0,\beta_0,\gamma_0)_{n_2=0}. \qquad (132)$$

For interchanges $n_1\leftrightarrow n_2$, $n_3\leftrightarrow n_4$, the sum $\Sigma_0$ should obviously be invariant. However, as a result of these interchanges the quantity $\beta_0$ in the summand changes sign while $\alpha_0$ and $\gamma_0$ remain unchanged. Consequently, the third part of $\Sigma_0$ (involving an odd function of $\beta_0$) would identically vanish. The corresponding parts of $\Sigma_1$ and $\Sigma_2$ give

$$2\bar{a}^2mm^*(m+m^*)(2\pi\beta)^{-5/2}\{m^{*-1/2}F_1+m^{-1/2}F_2], \qquad (133)$$

where

$$F_1=\sum_{n_1,n_2,n_3=1}^{\infty}(n_1n_2n_3)^{-1/2}(n_1+n_2)^{-1}\frac{n_1+\zeta n_2}{n_1(n_2+n_3)+\zeta^2n_2(n_3-n_1)}z^{n_1+n_2}z^{*n_3},$$

and

$$F_2=\sum_{n_1,n_3,n_4=1}^{\infty}(n_1n_3n_4)^{-1/2}(n_3+n_4)^{-1}\frac{n_3-\zeta n_4}{n_3(n_1+n_4)+\zeta^2n_4(n_1-n_3)}z^{n_1}z^{*n_3+n_4},$$

with

$$\zeta=(m-m^*)/(m+m^*).$$

The remaining parts of $\Sigma_0$, $\Sigma_1$, and $\Sigma_2$ may now be combined, with the result

$$\Sigma=\sum_{\substack{n_1,n_3=1\\ n_2,n_4=0}}^{\infty}\frac{(\alpha_0+\beta_0+\gamma_0)^{1/2}-(\alpha_0)^{1/2}}{(\beta_0/2)^2-\alpha_0\gamma_0}z^{n_1+n_2}z^{*n_3+n_4}-\sum_{n_1,n_3=1}^{\infty}\frac{(\alpha_3+\beta_3+\gamma_3)^{1/2}-(\alpha_3)^{1/2}}{(\beta_3/2)^2-\alpha_3\gamma_3}z^{n_1}z^{*n_3}, \qquad (134)$$

with

$$(\alpha_3,\beta_3,\gamma_3)=(\alpha_0,\beta_0,\gamma_0)_{n_2=n_4=0}. \qquad (135)$$

Now, the first part of the quadruple sum in $\Sigma$ becomes, under the transformation

$$n_1=n_1'+1,\quad n_2=n_2'-1,$$
$$n_3=n_3'+1,\quad n_4=n_4'-1,$$

$$\sum_{\substack{n_1',n_3'=0\\ n_2',n_4'=1}}^{\infty}\frac{(\alpha_0')^{1/2}}{(\beta_0'/2)^2-\alpha_0'\gamma_0'}z^{n_1'+n_2'}z^{*n_3'+n_4'},$$

where $\alpha_0'$, $\beta_0'$ and $\gamma_0'$ are the same functions of $n_1'$, $n_2'$,

$n_3'$, and $n_4'$ as $\alpha_0$, $\beta_0$ and $\gamma_0$ are of $n_1$, $n_2$, $n_3$, and $n_4$. Because of the symmetry of the summand with respect to the interchanges of suffices $1 \leftrightarrow 2$, $3 \leftrightarrow 4$, the foregoing sum would exactly cancel with the second part of the quadruple sum in $\Sigma$. We are thus left with only the double sum in (134) which is found to be

$$-4(m+m^*)^{-3/2} \sum_{n_1, n_3=1}^{\infty} (n_1 n_3)^{-2} \left( n_1 n_3 - \frac{m n_1 + m^* n_3}{m+m^*} \right)^{1/2} z^{n_1} z^{*n_3}. \tag{136}$$

Introducing the constants appearing in (126), this gives

$$-4\bar{a}^2 m m^* (m+m^*)^{1/2} (2\pi\beta)^{-5/2} \sum_{r,s=1}^{\infty} (rs)^{-2} \left( rs - \frac{mr + m^* s}{m+m^*} \right)^{1/2} z^r z^{*s}. \tag{137}$$

The final result for the integral $I$ is then equal to the sum of (133) and (137).

PHYSICAL REVIEW VOLUME 129, NUMBER 2 15 JANUARY 1963

# Quantum Cell Model for Bosons

H. A. GERSCH AND G. C. KNOLLMAN*
*School of Physics, Georgia Institute of Technology, Atlanta, Georgia*
(Received 2 August 1962)

An approach is presented toward validating the assumption that the ground state of bosons with repulsive interactions at low densities is characterized by macroscopic occupation of the zero momentum level. We use a cell model which affords a simple description of the high-density region, where fluctuations in number density are small and where no single-particle level is macroscopically occupied. As the density decreases, fluctuations increase, and we reach a critical density at which the small fluctuation approximation becomes unstable with respect to plane wave states of zero momentum. At this critical density, the single-particle energy gap disappears, and the dependence of excitation energy on momentum changes from quadratic to linear, for small values of momentum.

## I. INTRODUCTION

THE model of $N$ hard-sphere bosons at low densities has been very successful in predicting many of the physical properties of a superfluid.[1] Of significance in theoretical treatments is the role played by the assumption that in the presence of the repulsive interactions a finite fraction of particles occupy the state with zero linear momentum. In the second quantized formulation of the model, this assumption facilitates reduction of the Hamiltonian operator from quadrilinear to quadratic form in plane wave creation and destruction operators.[1] In a configurational-space approach, it enables one to calculate the effects of interaction using the ring integrals of Mayer cluster theory.[2]

This assumption regarding a macroscopically occupied level is physically plausible for repulsive interactions at low particle densities. Moreover, it provides a self-consistent theoretical development, that is, once it is invoked, the theory shows that the interactions do not destroy the macroscopic single level occupation. However, the validity of the assumption has never been proved.

Our aim here is to attempt to indicate with a simplified model how the condensation in momentum space may result spontaneously from the theory without having to assume it at the outset. Such is the state of affairs in the treatment of thermodynamic properties characterizing an ideal Bose gas.[3] There, at sufficiently high temperatures, no single-particle level is macroscopically occupied. As the temperature is decreased below a critical value, the requirement concerning a fixed number of particles comprising the system forces a finite fraction of the particles to occupy the lowest momentum level. One thus obtains a complete description of the ideal gas of bosons in both the region of no macroscopic occupation of a single-particle level (normal region) and the region of macroscopic occupation of the single-particle zero momentum level (superfluid region). It would, of course, be pleasing to have the same complete description for bosons with repulsive interactions. We have not developed such an inclusive treatment in this work, but rather have observed the ground state of the system starting from

* Present Address: Lockheed Missiles and Space Company, Palo Alto, California.

[1] N. N. Bogoliubov, J. Phys. (U.S.S.R.) **2**, 23 (1947); K. A. Brueckner and K. Sawada, Phys. Rev. **106**, 1117 (1957); T. D. Lee, K. Huang, and C. N. Yang, *ibid.* **106**, 1135 (1957).

[2] H. A. Gersch and V. H. Smith, Phys. Rev. **119**, 886 (1960).

[3] F. London, Phys. Rev. **54**, 948 (1938).